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# Electrical conductivity and local structure of barium manganese iron vanadate glass

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**Abstract** Local structure and electrical conductivity of semiconducting $20BaO{\cdot}10Fe_2O_3 \cdot x\,MnO_2 \cdot (70-x)V_2O_5$ glass ($x = 0-30$), abbreviated as $x$BFMV, were investigated by means of $^{57}$Fe-Mössbauer spectroscopy, differential thermal analysis (DTA) and DC four-probe method. Mössbauer spectrum of these vanadate glasses consists of a doublet with an identical isomer shift ($\delta$) of 0.38±0.01 mm s$^{-1}$, indicating that distorted $FeO_4$ tetrahedra constitute the structural units with distorted $VO_4$ tetrahedra and $VO_5$ pyramids. Quadrupole splitting ($\Delta$) gradually increases from 0.70±0.02 to 0.87±0.02 mm s$^{-1}$ with an increase in the $MnO_2$ content, indicating an increased local distortion of $Fe^{III}O_4$ tetrahedra. DTA study of these glasses showed a gradual increase of glass transition temperature ($T_g$) from 329±5 to 411±5°C, showing an improved thermal durability. '$T_g$ vs. $\Delta$ plot' yielded a straight line with a large slope of 707°C(K)/mm s$^{-1}$, proving that $Fe^{III}$ played a role of network former (NWF). An isothermal annealing of 10BFMV glass at 500°C for 1000 min resulted in a marked increase in the electrical conductivity ($\sigma$) from (4.5±3.9) × 10$^{-7}$ to (1.4±0.3) × 10$^{-2}$ S cm$^{-1}$ and a decrease in the activation energy for the electrical conduction ($E_a$) from 0.33 ± 0.07 to 0.11±0.01 eV, while $\Delta$ of $Fe^{III}$ decreased from 0.76±0.02 to 0.49±0.02 mm s$^{-1}$. These results suggest that decrease

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in the distortion of $Fe^{III}O_4$ tetrahedra involved with the structural relaxation causes an increase in the probability of electron hopping from $V^{IV}$ or $V^{III}$ to $V^{V}$.

**Keywords** Barium manganese iron vanadate glass · $^{57}$Fe-Mössbauer spectroscopy · Electrical conductivity · Structural relaxation

## 1 Introduction

Vanadate glass is known to be a semiconductor with an electrical conductivity ($\sigma$) of $10^{-7}$–$10^{-5}$ S cm$^{-1}$. The electrical conduction is known to be caused by polaron hopping from $V^{IV}$ or $V^{III}$ to $V^{V}$ [1]. A drastic increase in $\sigma$ was discovered in annealed barium iron vanadate glass [2] having a registered trademark of '*NTA glass*™' in Japan. Nishida reported a large charge-discharge capacity of 150 mAh g$^{-1}$ in lithium-ion battery (LIB) in which cathode active material of annealed vanadate glass, $Li_2O$-$Fe_2O_3$-$V_2O_5$-$P_2O_5$, was used successfully [3]. This result indicates that vanadate glass could be a good candidate for the cathode active material of LIB. In the present study, substitution of manganese for vanadium was investigated in barium iron vanadate glass, BaO-$Fe_2O_3$-$V_2O_5$, in order to investigate the relationship between the local structure and the conductivity.

## 2 Experimental

Vanadate glasses with a composition of $20BaO{\cdot}10Fe_2O_3 \cdot x MnO_2{\cdot}(70\text{-}x)V_2O_5$, abbreviated as *x*BFMV, were prepared by a conventional melt-quenching method. Weighed amounts of $BaCO_3$, $Fe_2O_3$, $MnO_2$ and $V_2O_5$ of reagent grade were well mixed in a mortar and melted at 1200°C for 1 h in an electric muffle furnace. Homogeneous dark brown glass samples could be prepared when '*x*' was equal to or less than 30. Enriched isotope of $^{57}Fe_2O_3$ ($^{57}$Fe = 95.54 %) was used for some sample preparation. Isothermal annealing was carried out at 500°C for 1000 min. Mössbauer measurement was performed by a constant acceleration method with a source of $^{57}$Co(Rh) and a reference of $\alpha$-Fe foil for isomer shift ($\delta$). DTA was conducted from RT to 500°C under a heating rate of 10°C min$^{-1}$ by using 10 mg of finely pulverized glass sample. $\alpha$-$Al_2O_3$ was used as a reference of the temperature. Values of $\sigma$ were measured at temperatures ranging from 30 to 125°C by dc-four probe method under the electric current from −1.0 to 1.0 mA.

## 3 Results and discussion

Mössbauer spectra of 10BFMV glass measured before and after isothermal annealing at 500°C for 1000 min, are shown in Fig. 1. When '*x*' was increased from 0 to10, 20 and 30, consistent $\delta$ value of 0.38±0.01 mm s$^{-1}$ were observed, while quadrupole splitting ($\Delta$) increased from 0.70 to 0.76, 0.79 and 0.87±0.02 mm s$^{-1}$. These results indicate that $Fe^{III}$ atoms form distorted $Fe^{III}O_4$ tetrahedra, and that they became more distorted when $MnO_2$ was substituted for $V_2O_5$. In annealed samples, a marked decrease in $\Delta$ was observed like 0.52 ($x = 0$), 0.49 ($x = 10$) and 0.43±0.02 mm s$^{-1}$ ($x = 20$), showing a largely decreased local distortion of $FeO_4$

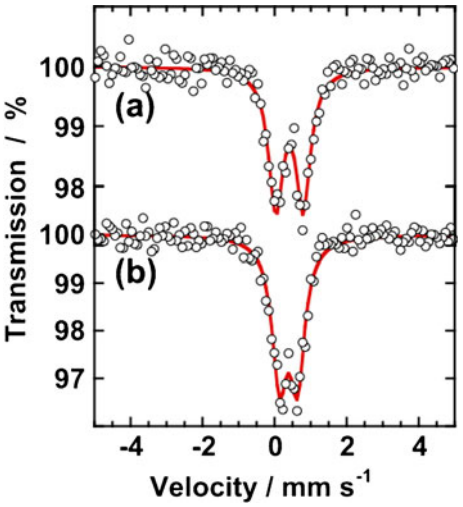


**Fig. 1** Mössbauer spectra of $20BaO{\cdot}10Fe_2O_3{\cdot}10\ MnO_2{\cdot}60\ V_2O_5$ glass of (**a**) before and (**b**) after isothermal annealing conducted at 500°C for 1000 min

tetrahedra involved in the structural relaxation. In case of annealed sample with $x$ of 30, $\Delta$ of 0.54±0.02 mm $s^{-1}$ was observed, which is slightly larger than other annealed samples. This can be explained by the difference in the ionic radius of $Mn^{IV}$ (39 pm) that is much smaller than that of $V^{IV}$ (53 pm) [4]. It is considered that oxygen atoms constituting the network will be intensively attracted to $Mn^{IV}$ in both as-quenched glass and annealed samples. Large $\Delta$ of 0.87±0.02 mm $s^{-1}$ obtained for as-quenched glass sample supports this idea. We can describe that chemical property of "vanadate glass" is predominantly observed when $MnO_2$ content is equal to or less than 20 mol%.

DTA curves of $x$BFMV glass are depicted in Fig. 2. A gradual increase in glass transition temperature ($T_g$) was observed from 329 to 347, 372 and 411±5°C, while that in crystallization temperature ($T_c$) from 378 to 400, 429 and 465±5°C. A linear relationship found between $T_g$ and $\Delta$ of $Fe^{III}$ was termed '$T_g$-$\Delta$ rule' [5], *i.e.*:

$$T_g = a\Delta + b \tag{1}$$

where $a$ and $b$ are slope and intercept of the straight line, respectively. According to the '$T_g$-$\Delta$ rule' [5], large '$a$' value of 680°C(K)/mm $s^{-1}$ is generally obtained when $Fe^{III}$ is located at tetrahedral site as network former (NWF), whereas '$a$' becomes only 35°C(K)/mm $s^{-1}$ when $Fe^{III}$ is located at octahedral site as network modifier (NWM). In the present study, a large '$a$' of 707°C(K)/mm $s^{-1}$ was obtained, indicating that $Fe^{III}$ atoms occupy tetrahedral site as NWF.

A slight decrease in $\sigma$ value from (2.5±1.2) × $10^{-6}$ to (4.7±3.8) × $10^{-7}$, (4.2±0.3) × $10^{-7}$ and (2.3±1.0) × $10^{-7}$ S $cm^{-1}$ was observed when the '$x$' value of $x$BFMV glass increased from 0 to 10, 20, and 30. These results will be due to decrease in number of carriers ($V^{IV}$or $V^{III}$) when $MnO_2$ was substituted for $V_2O_5$. In the case of 10BFMV glass, a marked increase in $\sigma$ was observed from (4.7±3.8) × $10^{-7}$ to (1.4±0.3) × $10^{-2}$ S $cm^{-1}$ after the annealing. According to the small polaron hopping theory [1], temperature dependence of $\sigma$ is expressed by:

$$\sigma T = \sigma_0 \exp(-E_a/kT), \tag{2}$$

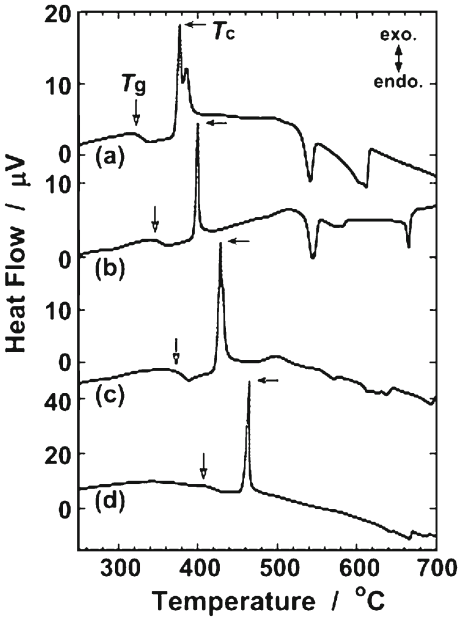


**Fig. 2** DTA curves of $20BaO{\cdot}10Fe_2O_3 \cdot xMnO_2 \cdot (70-x)V_2O_5$ glasses with '$x$' of (**a**) 0, (**b**) 10, (**c**) 20 and (**d**) 30, recorded at a heating rate of 10°C/min

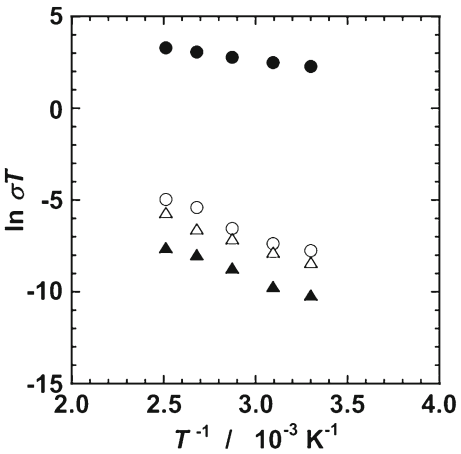


**Fig. 3** $\ln \sigma T$ *vs.* $1/T$ plot of $20BaO{\cdot}10Fe_2O_3 \cdot xMnO_2 \cdot (70-x)V_2O_5$ glasses with $x$ of 10 (circle) and 30 (triangle) measured before annealing (open symbols) and after isothermal annealing conducted at 500°C for 1000 min(closed symbols)

where $E_a$ and $k$ are activation energy for electric conduction and Boltzmann constant, respectively. As shown in Fig. 3, a drastic decrease in the $E_a$ from 0.33±0.07 to 0.11±0.01 eV was observed after the annealing of 10BFMV glass. On the other hand, a constant $E_a$ value of 0.29±0.06 eV was obtained in the case of 30BFMV glass. It is interesting that the decrease in the local distortion of $Fe^{III}O_4$ tetrahedra and a marked increase in the conductivity are clearly observed when '$x$' is 10 or less, *i.e.*, the distortion of network involved with an increase in $\sigma$ is intrinsic the vanadate glass.

## 4 Summary

Structure of *x*BFMV glass with *x* of 0, 10, 20 and 30 was investigated by means of $^{57}$Fe-Mössbauer and DTA. $Fe^{III}$ atoms are incorporated in the glass matrix to form distorted $FeO_4$ tetrahedra, and play a role of NWF at the substitutional sites of $VO_4$ tetrahedra by sharing corner oxygen atoms with each other. Electrical conductivity of 10BFMV glass increased from $4.7 \times 10^{-7}$ to $1.4 \times 10^{-2}$ S cm$^{-1}$ after isothermal annealing conducted at 500°C for 1000 min. Increase in the conductivity is ascribed to a decrease in the distortion of $VO_4$ and $FeO_4$ units constituting the glass network, accompanied by a decrease in the activation energy for the electron hopping ($E_a$) from 0.33 to 0.11 eV, and an increased probability of polaron (3d-electron) hopping from $V^{IV}$ or $V^{III}$ to $V^{IV}$.

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